भारतीय मानक
Indian Standard

IS 17539 : 2021

सिल्वर कैटालिस्ट — विशिष्टि

Silver Catalyst — Specification

ICS 71.060

© BIS 2021

भारतीय मानक ब्यूरो
BUREAU OF INDIAN STANDARDS
मानक भवन, 9 बहादुरशाह ज़फर मार्ग, नई दिल्ली – 110002
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI-110002
www.bis.gov.in www.standardsbis.in

March 2021 **Price Group 6**

Inorganic Chemicals Sectional Committee, CHD 01

FOREWORD

This Indian Standard is formulated by the Bureau of Indian Standards after the draft finalized by the Inorganic Chemicals Sectional Committee had been approved by the Chemical Division Council.

This standard deals with silver catalysts which are majorly used in oxidation reactions. It is used in industries for the production of formaldehyde and ethylene oxide. Silver catalyst used for the production of formaldehyde is in the form of crystals that has a thin porous coating of oxidic material of elements. On the other hand, silver catalyst that is used for ethylene oxide production consists of about 15 percent silver doped on α-alumina surface.

The composition of committee responsible for the formulation of this standard is given at Annex B.

For the purpose of deciding whether a particular requirement of this standard is complied with the final value, observed or calculated, expressing the result of a test or analysis shall be rounded off in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

Indian Standard

SILVER CATALYST — SPECIFICATION

1 SCOPE

This standard covers the requirements and methods of test for silver metal catalyst. The material is used in the production of formaldehyde and ethylene oxide at industrial level.

2 REFERENCES

The Indian Standards given below contain provisions which through reference in this text, constitute provision of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards.

IS No.	*Title*
265 : 1993	Hydrochloric acid — Specification (*fourth revision*)
266 : 1993	Sulphuric acid (*third revision*)

3 GRADES

There shall be two grades of silver catalyst as follows:

a) *Grade 1* — Generally used in the production of ethylene oxide.

b) *Grade 2* — Generally used in the production of formaldehyde.

4 REQUIREMENTS

The material shall be in crystalline form free from dirt, foreign matter and material shall correspond in composition essentially to silver metal crystals doped on alumina (Grade 1), silver metal crystals or silver gauge (Grade 2).

5 DESCRIPTION

The material shall also comply with the requirements prescribed in Table 1 when tested according to the methods prescribed in Annex A.

6 PACKING AND MARKING

6.1 Packing

The material shall be packed in suitable dark coloured airtight containers as agreed to between the purchaser and the supplier.

6.2 Marking

6.2.1 Each package shall be marked with the following information:

a) Name of the material,

b) Name of the manufacturer and address,

c) Net mass of contents,

d) Lot number,

e) Date of manufacture,

f) Expiry date, and

g) Hazard warning Symbols.

6.2.2 *BIS Certification Marking*

The product(s) conforming to the requirements of this standard may be certified as per the conformity assessment schemes under the provisions of the *Bureau of Indian Standards Act*, 2016 and the Rules and Regulations framed thereunder, and theproducts may be marked with the Standard Mark.

Table 1 Requirements for Silver Catalyst

(*Clause* 5)

Sl No.	Characteristic	Requirements		Annex
		Grade-1	Grade-2	
i)	Bulk density (g/cm^3)	1.2-1.5	1.7-2.0	A-1
ii)	Silver (as Ag, percent by mass, *Min*)	15	99.9	A-2
iii)	Lead (as Pb, ppm *Max*)	20	10	A-3 and A-7
iv)	Iron (as Fe, ppm *Max*)	30	10	A-4 and A-7
v)	Copper (as Cu, ppm, *Max*)	10	10	A-5
vi)	Nitrate (percent by mass, *Max*)	0.01	–	A-6
vii)	Alumina (percent by mass, *Max*)	85	–	A-8
viii)	Surface area (m^2/g)	0.5-5 or as agreed between the parties	5-10 or as agreed between the parties	A-9

ANNEX A

(*Clause* 5)

A-1 BULK DENSITY

A-1.1 Procedure

Transfer the material as received and pour slowly in a 250 ml stoppered measuring cylinder up to 50 ml mark without knocking. Level the top bed of surface to the mark by gently lifting the cylinder as far as 5 cm from the base pad and releasing it to allow free fall to knock the pad. Repeat this knocking for 4 more times. Add further 50 ml of the sample and knock five times, as above, after every 50 ml addition up to 250 ml. Level the cylinder with the material without any further knocking. Empty out the material from the cylinder and weigh to the nearest 0.5 g. Then heat the sample in an unventilated oven at 250 ± 5 °C for 3 h. Place the cylinder in a desiccator, cool and weigh to constant mass.

A-1.2 Calculation

$$\text{Bulk density, g/cm}^3 = 0.004\ \text{M}$$

where

M = mass, in g, of the material in the cylinder.

A-2 DETERMINATION OF SILVER

A-2.1 Reagent

A-2.1.1 *Dilute Hydrochloric Acid*, approximately 5 N.

A-2.2 Procedure

Weigh accurately about 1 g of the material and dissolve in 150 ml of water, heat to boiling and add slowly with constant stirring 2 ml of hydrochloric acid. Boil until the precipitate coagulates and set aside to cool in dark for atleast 4 h, preferably overnight. Filter through a tared sintered glass crucible (G. No. 4) and wash the precipitate with cold water until free from chloride. Dry the precipitate at 130 °C ± 2 °C to constant mass.

2.3 Calculation

$$\text{Silver (as Ag, percent by mass)} = \frac{118.5 \times M_1}{M_2}$$

where

M_1 = mass in g, of the precipitate; and

M_2 = mass in g, of the material taken for the test.

A-3 TEST FOR LEAD (as Pb)

A-3.1 Method A

A-3.1.1 *General*

The colour developed by the material with sodium sulphide solution is compared with that of a control solution.

A-3.1.2 *Apparatus*

A-3.1.2.1 *Nessler Cylinder,* 50 m1 capacity.

A-3.1.3 *Reagents*

A-3.1.3.1 *Ammonium Hydroxide,* 5 N.

A-3.1.3.2 *Dilute Acetic Acid,1:1.*

A-3.1.3.3 *Sodium Sulphide Solution,* 12 percent *(m/v).*

A-3.1.3.4 *Standard Lead Solution* — Dissolve 0·160 g of lead nitrate in 90 ml of water to which 1 ml of nitric acid has been added, and dilute to 100 ml. Keep this solution in lead-free stoppered bottle. Further dilute 10 ml of this solution with water to 1 000 ml. One millilitre of this solution contains 0.01 mg of lead (as Pb).

A-3.1.4 *Procedure*

Dilute 1.2 ml/2.0 g of the material with 10 ml of water in a 150 ml beaker, neutralize with ammonium hydroxide solution, add sufficient dilute acetic acid to render the solution acidic. Transfer this solution to a 50 ml Nessler cylinder and dilute with water to mark and add 0.5 to 1 ml of sodium sulphide solution. Carry out a control test using 2 ml of standard lead solution, 5 ml of dilute acetic acid in a 50 ml Nessler cylinder diluting to mark with water and adding 0.5 to 1 ml of sodium sulphide solution.

A-3.1.4.1 The limit prescribed in Table 1 shall be taken as not having been exceeded if the intensity of colour produced with the material is not greater than that produced in the control test.

A-3.2 Method B (Spectroscopic Method)

A-3.2.1 *Principle*

A sample containing microgram quantities of lead is extracted with dithizone solution in chloroform. The extraction is carried out in the presence of strong ammoniacal citrate-cyanide reducing agent (*p*H 10 to 11.5). The quantity of lead present in the sample is determined spectrophotometrically by measuring the absorbance at 510 nm in chloroform extract containing the lead dithizonate complex.

A-3.2.2 *Minimum Detection Limit*

1.0 µgPb/10 ml dithizone solution (extract).

A-3.2.3 Apparatus

A-3.2.3.1 *Spectrophotometer*, for use at 510 nm with a path length of 1 cm or longer.

A-3.2.3.2 *pH meter*

A-3.2.3.3 *Standard volumetric glasswares*

A-3.2.3.4 *TEF beaker,* 100 ml for acid digestion.

A-3.2.3.5 *Separatory funnels,* 250 ml and 500 ml.

All glasswares are to be cleaned with 1 : 1 HNO_3, and rinsed thoroughly with distilled water.

A-3.2.4 *Reagents*

A-3.2.4.1 *Quality of reagents*

Only analytical or equivalent grade reagents, unless specified otherwise, are to be used. All reagents are to be prepared in lead-free distilled water.

A-3.2.4.2 *Stock lead solution*

Dissolve 0.159 9 g lead nitrate [($Pb(NO_3)_2$, minimum purity, 99.5 percent (*w/w*)] in about 200 ml of water. Add 10 ml concentrated HNO_3 and dilute to 1000 ml with water, 1.0 ml of this solution will contain 100 µg of Pb.

A-3.2.4.3 *Standard lead solution*

Dilute 2.0 ml of stock lead solution to 100 ml with water, 1.0 ml of this solution will contain 2 µg of Pb.

Nitric Acid — Concentrated (18N).

Nitric Acid — Dilute — 20 percent, *v/v*.

Ammonium Hydroxide — Concentrated (14N).

Ammonium Hydroxide — Dilute 10 percent, *v/v* and 1 percent, *v/v.*

Citrate-Cyanide Reducing Solution — Dissolve 200 g anhydrous ammonium citrate [$(NH_4)_2\ HC_6H_5O_7$] 10 g anhydrous sodium sulphite (Na_2SO_3), 5 g hydroxylamine hydrochloride, 20 g potassium cyanide (KCN) in water and dilute to 500 ml, and mix with one litre of concentrated NH_4OH.

CAUTION — KCN is a poisonous solution. Handle with extreme care and do not pipette by mouth.

A-3.2.4.4 *Stock dithizone solution*

Dissolve 25 mg dithizone in about 50 ml chloroform ($CHCl_3$) taken in a 200 ml beaker and filter through Whatman No. 42 (or equivalent) filter paper. Collect the filtrate and two washings (10 ml each) in a 250 ml conical flask. Transfer the combined filtrate to a 500 ml separatory funnel. Add about 100 ml 1 percent (*v/v*) NH_4OH solution, shake moderately for about 1 min. Transfer the $CHCl_3$ layer to another 250 ml separatory funnel retaining the orange-red aqueous layer in the 500 ml separatory funnel. Repeat the extraction (of the $CHCl_3$ layer) with 100 ml of 1 percent (*v/v*) NH_4OH solution, transfer the $CHCl_3$ layer to another 250 ml separatory funnel and the aqueous layer to the original 500 ml separatory funnel containing the first extract. One more repetition, of extraction and transferring to the main aqueous layer is carried out. To the combined aqueous extract in the 500 ml separatory funnel add 1 : 1 HC1 in 2 ml portions, mixing after each addition, until dithizone precipitation is complete and the solution is no longer orange-red. Extract the precipitated dithizone with three 25 ml portions of $CHCl_3$. Dilute the combined extract to 250 ml with $CHCl_3$, 1 ml of this solution will contain 100 µg of dithizone.

A-3.2.4.5 *Working dithizone solution*

Dilute 100 ml stock dithizone solution to 250 ml in a standard volumetric flask with $CHCl_3$, 1 ml of this solution will contain 40 µg of dithizone.

A-3.2.5 *Procedure*

A-3.2.5.1 *Sample digestion*

Digest all samples for lead as per standard digestion procedure using minimum amount of HNO_3-H_2SO_4 and HNO_3-$HClO_4$. Dilute the acidified sample (*p*H = 2) to 100 ml and add 20 ml of dilute (20 percent, *v/v*) HNO_3, filter if required through a filter paper (Whatman No. 41 or equivalent), and transfer it to a 250 ml separatory funnel. Add 60 ml ammoniacal citrate-cyanide solution, mix and cool to room temperature. Add 10 ml of dithizone working solution. Shake the stoppered funnel vigorously for about 30 s, allow to stand (to get two separate layers). Discard 1-2 ml $CHCl_3$ layer and then fill the absorption cell. Measure the absorbance at 510 nm using working dithizone solution as reagent blank.

A-3.2.5.2 *Calibration curve*

Plot a calibration curve using at least five standard lead solutions, after adding 50 ml ammoniacal citrate-cyanide solution to the individual lead standard solutions and extracting the same with 10 ml of dithizone working solution.

A-3.2.6 *Calculation*

mgPb/litre = µg (in 10 ml extract obtained from calibration curve)/Volume of sample (ml).

A-3.3 Alternative Method

Lead may alternatively be estimated by the instrumental method as given at **A-7**.

A-4 TEST FOR IRON

A-4.1 General

Trivalent iron is reduced by means of hydroxyl-ammonium chloride and a bivalent iron−2, 2’-bipyridyl complex at *p*H 3.1, at a temperature of 75 °C is formed. Photometric measurement of thecoloured complex is done at a wavelength of about 520 nm.

A-4.2 Apparatus

A-4.2.1 *p*H *Meter, fitted* with glass electrode.

A-4.2.2 Spectrophotometer, provided with a 1 cm cell.

A-4.3 Reagents

A-4.3.1 *Concentrated Hydrochloric Acid, see* IS 265.

A-4.3.2 *2,2'-Bipyridyl Solution* — Dissolve 0.50 g of 2, 2'-bipyridyl in 10 ml of concentrated hydrochloric acid and dilute to 100 ml with water.

A-4.3.3 *Ammonium Acetate Solution* — Dissolve 300 g of ammonium acetate in water and make the volume to 1 000 ml.

A-4.3.4 *Hydroxylammonium Chloride* — Dissolve 10 g of hydroxyl-ammonium chloride ($NH_2OH.HC1$) in water and dilute to 100 ml.

A-4.3.5 *Standard Iron Solution* — Dissolve 0.702 g of ferrous ammonium sulphate [$Fe\,(NH_4)_2(SO_4)_2.6H_2O$] in 20 ml of 10 percent sulphuric acid and dilute with water to exactly 500 ml. Further dilute 100 ml of this solution to 1000 ml. One millilitre of the diluted solution is equivalent to 0.02 mg of iron (as Fe).

A-4.4 Procedure

A-4.4.1 *For Technical and Reagent Grade*

A-4.4.1.1 *Preparation of sample solution* — Weigh 50 g of the material to the nearest 0.01 g in a small glass beaker. Transfer quantitatively to a 500 m1 volumetric flask and make up to the mark with carbon dioxide-free water. Mix and use the sample solution for tests. Pipette out 5 ml of the sample solution in a 100 m1 volumetric flask and dilute to the mark. Shake the contents. This diluted solution shall be called the diluted sample solution.

A-4.4.1.2 *Blank test* — At the same time as the analysis, carry out a blank test using the procedure described in **A-4.4.1.4** and the same quantities of all reagents.

A-4.4.1.3 *Preparation of calibration curve* — Proceedthe method as prescribed below:

a) *Preliminary Check of p*H — Place 5 ml of concentrated hydrochloric acid in a beaker of suitable capacity (for example, 100 ml), dilute to approximately 50 ml, add 1 ml of hydroxylammoniumchloride solution and 5 ml of 2, 2'-bipyridyl solution. Allow to stand for about ten minutes and using the *p*H meter, adjust the *p*H of the solution to 3.1 by addition of ammonium acetate solution. Note the quantity of ammonium acetate added for the *p*H adjustment and then discard the solution.

b) *Preparation of Standard Solutions* — Into each of a series of five beakers of suitable capacity (for example, 100 ml), place the quantities of standard iron solution indicated below:

Standard Iron Solution (ml)	**Corresponding to Iron (Fe)** (μg)
*0	0
5.0	100 (5.0 × 0.02 mg = 0.1 mg)
10.0	200 (10.0 × 0.02 mg = 0.2 mg)
15.0	300 (15.0 × 0.02 mg = 0.3 mg)
25.0	500 (25.0 × 0.02 mg = 0.5 mg)

*Compensation solution

Then add 5 ml of concentrated hydrochloric acid and dilute to approximately 50 ml.

c) *Colour Development* — To each of the above-mentioned solutions, add 1 ml of hydroxylammonium chloride solution and 5 ml of 2, 2'-bipyridyl solution. Allow to stand for about ten minutes, then add the quantity of ammonium acetate solution following the procedure of **A-4.4.1.3(a)** for adjusting *p*H of 3.1. Heat the solutions on a water-bath at approximately 75 °C for about fifteen minutes and then cool to room temperature. Transfer to 100 ml one-mark volumetric flasks, dilute to the mark and mix thoroughly.

d) *Photometric Measurement* — Measure the optical density of each solution using the spectrophotometer at a wavelength of about 520 nm, adjusting the instrument to zero optical density using as reference the compensation solution.

e) *Preparation of Calibration Graph* — Prepare a calibration graph for iron (Fe) content in micrograms per 100 ml of the standard solution as abscissa and the corresponding values of optical density as ordinate.

A-4.4.1.4 *Determination*

Pipette out 10 ml of the diluted sample solution (*see* **A-4.4.1.1)** into a beaker of suitable capacity (100 ml) and dilute to approximately 50 ml. Add 1 ml of hydroxylammoniumchloride solution and 5 ml of 2, 2'-bipyridyl solution. Allow to stand for about ten minutes, then using the *p*H meter, adjust the *p*H of the solution to 3.1 by addition of ammonium acetate solution. Heat the solution on a water-bath to approximately 75 °C for about fifteen minutes and cool to room temperature. Transfer the solution quantitatively to a 100 ml one-mark volumetric flask, dilute to the mark and mix thoroughly. Measure the optical density of the solution adjusting the instrument to zero optical density with the blank test solution and following the procedure described in **A-4.4.1.3**(d).

A-4.4.1.5 *Calculation*

By reference to the calibration graph, read the iron content corresponding to the photometric measurement of the sample and calculate.as given below:

$$\text{Iron (as Fe), percent by mass} = \frac{A \times 100 \times 100}{E}$$

where

A = mass in g, of iron determined in the sample solution, and

E = mass in g, of the sample taken for the test in **A-4.4.1.1**.

A-4.5 Alternative Method

Iron may alternatively be estimated by instrumental method as given at **A-7**.

A-5 DETERMINATION OF COPPER

A-5.1 Method A

A-5.1.1 *Outline of Method*

Copper is determined colorimetrically by measurement of the colour produced by the material with zinc dibenzyldithiocarbomate. The value is read off from a standard calibration graph.

A-5.1.2 *Apparatus*

A-5.1.2.1 *Separating Funnels* — 100 ml capacity. Rinse the funnel with dilute hydrochloric acid and with water before use. Allow to drain, then dry the stems with pure absorbent cotton wool and place a small plug of cotton wool in each stem.

A-5.1.2.2 *Photoelectric Absorptiometer,* with 1 cm cells.

A-5.1.3 *Reagents*

A-5.1.3.1 *Ammonium Hydroxide ,* 10 N approximately.

A-5.1.3.2 *Dilute Hydrochloric Acid,* 5 N.

A-5.1.3.3 *Zinc dibenzyldithiocarbomate solution,* 0.04 percent solution in carbon tetrachloride.

A-5.1.3.4 *Standard copper solution* — Weigh 0.491 g of copper sulphatepentahydrate ($CuSO_4$, $5H_2O$) in a weighing bottle. Wash into a 250 m1 volumetric flask. Add 3 ml of 18 N sulphuric acid, dilute to about 100 ml, and swirl until the salt has completely dissolved. Dilute to the mark and mix well. This is the stock solution, one millilitre of which contains 0.5 mg of copper (Cu). Take 3 ml of 18 N sulphuric add andabout 200 ml of water in a 1 000 ml volumetric flask. Carefully pipette 5 ml of the stock copper solution into the flask. Dilute to the mark and mix well. One millilitre of this solution contains 2.5 µg of copper (Cu).

A-5.1.4 *Procedure*

A-5.1.4.1 Weigh accurately 5 g of the material into a 250 m1 beaker. Take a smaller mass if the copper is expected to exceed 3 parts per million. Add 30 ml of dilute hydrochloric acid and boil gently for 15 min. Place 30 ml of dilute hydrochloric acid in a second beaker as blank and continue with both. Allow to cool, then add ammonium hydroxide until the solution is alkaline to litmus paper. Add dilute hydrochloric acid dropwise until the solution is acidic, then add 3 ml in excess.

A-5.1.4.2 Transfer to a 100 m1 separating funnel and, if necessary, dilute to 50 ml. Add 10 ml of zinc dibenzyldithiocarbomate solution and shake vigorously for at least 2 min. Allow the layers to separate, thenunstopper the funnel, and run the lower layer through a plug of cotton wool into a l cm cell, using, the first few drops to rinse out the cell. Adjust the photometer at zero at 440 μm (blue photocell, plain glass filter) with a cell of zinc dibenzyldithiocarbomate solution in the light path, then measure the sample and the blank. Read off parts per million copper from the standard calibration graph.

A-5.1.4.3 *Standard calibration graph*

Take five 100 m1 separating funnels, and wash thoroughly with hydrochloric acid and then with water. In each funnel place 3 ml of dilute hydrochloric acid (5 N). Using pipettes or a micro burette, measure respectively: 0, 2, 5, 10 and 15 ml of standard copper solution. Dilute to 50 ml. Subtract a constant from each observed colorimeter reading so that the blank solution with no added copper corresponds to a reading of 0. Convert volumes of standard copper solution to micrograms of copper by multiplying by 2.5. Plot a graph with micrograms as ordinates and adjusted colorimeter readings as abscissae. Draw a line through the points and through the origin. Label the graph with particulars of cells and filters.

A-5.1.5 *Calculation*

$$\text{Copper (Cu), parts per million} = \frac{M_1}{M}$$

where

M_1 = mass in micrograms, of copper read off from the graph, and

M = mass in g, of the material taken for the test.

A-5.2 Method B

A-5.2.1 *Principle*

Copper present in the sample is reduced with the help of ascorbic acid and by addition of 2, 2’-biquinolyl forming a violet coloured complex.

A-5.2.2 *Reagents*

Sodium sulphate, hydrochloric acid solution, amyl alcohol, (+) tartaric acid, sodium hydroxide, L-ascorbic acid (100 g/l) , 2-2'biquinolyl (0.5 g/l), bromine water-saturated solution, copper (0.1 g/l), standard solution, indicator paper (narrow range) *p*H 5.5 to *p*H 7.0, methyl orange indicator (0.5 g/l) aqueous solution.

A-5.2.3 *Apparatus*

Spectrophotometer, photoelectric absorptiometer with maximum transmission at a wavelength of 545 nm, optical cells, 4 cm optical path.

A-5.2.4 *Procedure*

A-5.2.4.1 *Test portion*

Weigh about 10 g of the sample to the nearest 0.1 g.

A-5.2.4.2 *Preparation of the calibration graph*

Take six 500 ml separatory funnel and introduce the standard copper solutions.

Standard Copper Solutions

Standard Copper Solutions (ml)	Mass of Copper in µg
0	0
2	20
4	40
6	60
8	80
10	100

To all the funnels add 400 ml water and 2 ml of tartaric acid. *p*H of the solution is adjusted around 6.0 using sodium hydroxide. Add about 2 ml of ascorbic acid and mix the contents thoroughly. Allow the mixture to stand for 5 min. Add 2, 2'-biquinolyl solution (10 ml) and mix well. Now try to extract the copper complex using two 20 ml of amyl alcohol portions. Transfer the extract to 100 ml beaker. Add sodium sulphate (2 g) to extract and remove water traces by stirring thoroughly.

In the next step, filter dry extract into 50 ml one mark volumetric flask. Wash residual sodium sulphate using 2 ml two portions of amyl alcohol. Dilute the mark using amyl alcohol by transferring to volumetric flask and mix well.

Spectrophotometric Measurements

Measurements are made using spectrophotometer or photoelectric absorptiometer at a wavelength of 545 nm. Measurements are made using filters and adjusting the instruments properly to zero absorbance using amyl alcohol as blank solution.

A-5.2.4.3 *Determination*

Preparing Test solution

To a 400 ml beaker, transfer the test portion. Add 1 drop of methyl orange and 100 ml water. Using Hydrochloric acid, neutralize the solution adding 5 ml in excess. Add bromine water (10 ml) in excess and boil the solution till it is free from bromine. Allow the solution to cool. To a 500 ml seperatory funnel fitted with stopper, transfer the contents of the beaker and add 1 ml of HCl solution to it. After the sample preparation and colour development, photometric measurements are made on the test samples using blank test solution (by adjusting the instrument to zero absorbance).

A-5.2.4.4 *Calibration graph*

The graph for the above standard solutions is plotted between absorbance vs concentration. Take the absorbance of all the prepared solutions and then deduce the concentration of copper in the unknown solution using a calibration graph.

A-5.3 Expression of Results

Determine the concentration of copper corresponding to the absorbance value. The copper content expressed as mg/kg is given by:

$$\frac{m_1 - m_2}{1\,000} \times \frac{1\,000}{m_0} = \frac{m_1 - m_2}{m_0}$$

where

m_0 = is the mass of the test sample;

m_1 = is the mass of copper in test solution (in µg); and

m_2 = is copper in a blank solution.

A-6 TEST FOR NITRATES

A-6.1 General

The material is treated with brucine sulphate solution and the colour is compared with that of a control solution having known nitrate content.

A-6.2 Apparatus

A-6.2.1 *Spectrophotometer*

A-6.3 Reagents

A-6.3.1 *Brucine Sulphate Solution* — Dissolve 1 g of brucine sulphate in water and dilute to 100 ml.

A-6.3.2 *Standard Nitrate Solution* — Dissolve 0□162 9 g of potassium nitrate in water and dilute to 100 ml. Take 1 ml of this solution and dilute to 100 ml in another measuring flask. One millilitre of the diluted solution contains 0□01 mg of nitrate (as NO_3).

A-6.3.3 *Concentrated Sulphuric Acid — see* IS 266.

A-6.4 Procedure

Weigh 4.0 g of the material, dilute to 5 ml with water, add 2.5 ml of brucine sulphate solution, dilute to 10 ml and mix (solution A). Take separately 4.0 g of the material, dilute to 5 ml with water, add 2 ml of standard nitrate solution, 2.5 ml of brucine sulphate solution and dilute to 10 ml (solution B). Prepare a blank, diluting 2.5 ml of brucine sulphate solution to 10 ml (solution C).

A-6.4.1 Add with constant stirring and slowly (taking 20 to 30 s), 20 ml of concentrated sulphuric acid to solution A, B and C. Allow any transient red colour produced to change to yellow, then cool rapidly in an ice-bath to room temperature. When the solutions become cool, dilute to 50 ml with concentrated sulphuric acid. Set a spectrophotometer at 410 nm and adjust the instrument to read zero absorbance with solution C in the light path. Then determine the absorbance of solution A. Adjust the instrument to read zero absorbance with solution A in the light path, and determine the absorbance of solution B.

A-6.4.2 The limit prescribed in Table 1 shall be taken as not having been exceeded if the absorbance of solution A is not greater than that of solution B.

A-7 DETERMINATION OF LEAD AND IRON BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETER (ICP-OES) METHOD

A-7.1 Principle

The sample solution under analysis is nebulized through a nebulizer inside a spray chamber. The aerosol formed is aspirated to argon plasma torch [produced by a radio-frequency inductively coupled plasma (ICP)], where the molecules break into constituent atoms and/or molecular species and atoms get excited. These excited atoms then return back to the lower energy state by emitting radiation of specific wavelength. These emitted radiations are characteristic of an element and are measured by the Photomultiplier tube detector and intensity of such emitted radiation is directly proportional to the concentration of respective constituent element in the sample**.**

A-7.2 Recommended Wavelength, Limit of Quantification and Important Spectral Interferences

Elements along with the recommended wavelengths and typical estimated limits of quantification are listed in Table 2. Actual working detection limits are dependent on the type of instrumentation, detection device and sample introduction system used and on the sample matrix. Therefore, these concentrations can vary between different instruments. Additionally, Table 2 lists the most important spectral interferences at the recommended wavelengths for analysis.

A-7.3 Reagents and Solutions

A-7.3.1. *Nitric Acid (65 Percent) Suprapure*

A-7.3.2 *Standard Stock Solution* — Either Prepare by dissolving proportionate amount of soluble compounds of elements (preferably spectroscopic grade), or use commercially available certified stock solution of 10, 100 or 1 000 µg/ml of Lead, Iron in 2-5 percent nitric acid. It is preferable to prepare single stock solution of multi elemental standards for analysis.

A-7.3.3 *Standard Solution* — Pipette out 5 ml from 100 µg/ml standard stock solution into a 100 ml volumetric flask and make up volume with 2 percent nitric acid to prepare 5 µg/ml solution. From this 5 µg/ml solution, an aliquot of 1.0, 3.0 and 5.0 ml taken in 50 ml volumetric flasks (separate) and make up volume with 2 percent nitric acid to prepare 0.1, 0.3 and 0.5 µg/ml solution of respective elements under reference.

A-7.3.4 *Sample Preparation* — Weigh about 2.5 g of sample in a 50 ml volumetric flask and add 1.0 ml Nitric acid and make up the volume with water.

A-7.3.5 *Reagent Blank Solution* — Place 50 ml of nitric acid and 1 000 ml of water into an HDPE or PP container. For ultra-trace analysis, polytetrafluorethylene (PTFE) containers should be used. Prior to analysis, make sure that the acid matrix and concentration of the reagent blank solution is the same as in the standard and sample solutions.

A-7.4 Instrument

Set up the instrument as per the manufacturer's instructions manual for recommended operating parameters, based on the manufacturers operating manual and evaluated by internal check analysis using of standard solution of element as well as data selected carefully from Table 2.

A-7.5 Procedure

A-7.5.1 *Calibration*

Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the intermediate mixed standard solutions (*see* **7.3.3**). The relationship between concentration and intensity is linear up to six orders of magnitude. Examine the spectra of the element and make necessary adjustments (if required) for the exact peak positions and baselines to ensure proper measurements of the respective peak intensities.

Flush the system with the reagent blank solution between each standard.

Table 2 Recommended Wavelengths, Achievable Limits of Quantification for Different Configuration of Instruments and Important Spectral Interferences

(*Clause* A-7.2)

Sl No.	Element	Wavelength (nm)	Approx. Achievable limits		Interfering Elements
			Radial Viewing (µg)	Axial Viewing (µg)	
(1)	(2)	(3)	(4)	(5)	(6)
i)	Pb	220.353	14	5	Al, Co, Fe, Ti
		283.305	(70)	(20)	Cr, Fe
ii)	Fe	238.204	14	(3)	Co
		259.940	6	2	Co
		271.441	–	–	–

A-7.5.2 Before beginning the sample run, re-analyse the reference standard with the highest concentration as if it were a sample. Ensure that the concentration values do not deviate from the actual values by more than ± 5 percent (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

Begin the sample run by flushing the system with the reagent blank solution (*see* **7.3.5**) between each sample. It is recommended to analyse a calibration check solution and the calibration blank solution every 10 samples. Analyze the sample solution and calculate the concentration in µg/ml of the lead (and/or iron) in the sample solution.

A-7.6 Calculation

The mass concentrations for each element are determined with the aid of the instrument software by following steps.

a) Relate emission signals from calibration blank and calibration solutions with the signals from reference elements and establish a calibration plot.

b) Determine the mass concentrations of samples with the aid of the emissions and the calibration graphs and calculate the quantity in mg/kg of the constituent elemental impurities in the sample, by multiplying the value by 20 (dilution factor).

A-8 DETERMINATION OF ALUMINIUM OXIDE

A-8.1 Outline of the Method

From a aliquot of the main solution, alumina is determined complexometrically.

A-8.2 Reagents

A-8.2.1 *Caustic Soda* — 20 percent (m/v).

A-8.2.2 *Concentrated Hydrochloric Acid* — rd = 1.16.

A-8.2.3 *Sodium Carbonate* — Solid.

A-8.2.4 *EDTA (0.05 M)* — Dissolve about 18.64 g of the disodium salt of EDTA in water and transfer to a 1000 ml volumetric flask, dilute to the mark and mix.

A-8.2.5 *Methyl Red Indicator Solution* — 0.1 percent (m/v) in rectified spirit.

A-8.2.6 Dilute hydrochloric acid — 1 : 1 (v/v).

A-8.2.7 *Buffer Solution* (*p*H 5.3) — Dissolve 21.5 g of sodium acetate ($CH_3COONa.3H_2O$) in 300 ml water, add 2 ml glacial acetic acid and dilute to one litre.

A-8.2.8 *Standard Zinc Solution* (0.05 M) — Dissolve 3.26 g of electrolytic zinc granules (99.95 percent purity) in dilute hydrochloric acid (1 :1) and evaporate the solution to 1 to 2 ml, dilute with water, add 50 ml buffer solution (*p*H 5.3), mix and make up the volume to one litre. Standardize against standard aluminium solution following the method for determination of aluminium.

A-8.2.9 *Standard Aluminium Solution* (0.05 M) — Weigh accurately 1.3490 g of pure aluminium wire (99.9 percent) in a 500 ml beaker containing 50 ml of water and 50 ml concentrated hydrochloric acid. Heat the solution to dissolve the metal. Cool and dilute the solution to 1000 ml in a volumetric flask. (1 ml = 0.002 550 g $A1_20_3$).

A-8.2.10 *Xylenol Orange Solution* — Dissolve 0.5 percent (m/v) xylenol orange in water acidified with 2 drops of dilute hydrochloric acid (40 percent).

A-8.2.11 *Ammonium Fluoride-solid*

A-8.3 Procedure

A-8.3.1 Pipette out 50 ml aliquot from the main solution into 400 ml beaker and neutralize the solution with caustic soda solution. Dissolve the precipitate formed in minimum quantity of concentrated hydrochloric acid and pour the solution slowly with constant stirring to a 200 ml volumetric flask containing 25 ml of caustic soda solution and 1 g sodium carbonate. Keep this on the water-bath for about an hour and then cool to room temperature. Make up the volume to the mark with water and shake thoroughly. Filter dry and collect the filtrate in a dry beaker or dry polythene bottle.

A-8.3.2 Pipette out an aliquot (100 ml) from the filtrate to a 250 ml conical flask. Add about 30 ml of 0.05M EDTA solution and a drop of methyl red indicator. Neutralize the solution with dilute hydrochloric acid, add 15 ml buffer solution and boil the solution for about 2 min. Cool to room temperature and titrate with standard zinc solution using 2 to 3 drops of xylenol orange indicator. The colour changes from yellow to red. Add about 2 g of ammonium fluoride to the solution and boil the solution for about 2 min. Add 10 ml buffer solution cool to the room temperature and then titrate with standard zinc solution adding a drop of xylenol orange indicator. The end point is from yellow to pinkish red. The percentage of alumina is calculated from the titre value of second titration with zinc.

A-8.4 Calculation

$$\text{Alumina } (Al_2O_3), \text{ percent} = \frac{A \times B}{C} \times 100$$

A = ml of sample solution required for second titration,

B = equivalent Al_2O_3 (in g) per ml of sample solution, and

C = mass in g, of the sample as represented by the aliquot taken.

A-9 DETERMINATION OF SURFACE AREA

A-9.1 Apparatus

The apparatus consisting of the following is assembled as shown in Fig. 1.

A-9.2 Procedure

Connect the chamber, flow meters and nitrogen cylinder as shown in Fig. 1. Take the sample in the adsorption cell and regenerate it in the tubular furnace at 250 °C with dry air/nitrogen purge. Cool the sample in an empty desiccator. Adjust the two nitrogen flow inlets to get a partial pressure of 0.05 to 0.075 mm of Hg. Weigh the cooled sample and place it in the adsorption chamber. Carry out the adsorption for two hours till equilibrium is reached. Weigh the cell. Change the partial pressure of benzene to a higher value, say 0.125 to 0.150 and continue the adsorption by replacing the cell in the chamber for 1 h. Note four readings in the partial pressure range of 0.05 to 0.35 mm of Hg.

A-9.3 Calculation

BET equation is –

$$\frac{P/P_0}{g\left(1-\frac{P}{P_0}\right)} = \frac{1}{g_m C} + \frac{C-1}{g_m C}\, P/P_0$$

where

G = amount of benzene adsorbed at any P/P_o;

g_m = amount of adsorbate (benzene) required to form monolayer on the surface; and

C = constant.

If $\frac{P/P_o}{g\left(1-\frac{P}{P_o}\right)}$ is plotted against P/Po, a straight line (BET) plot is obtained in which slope = $C\text{-}1/g_m C$ and intercept = $1/g_m C$

Slope and Intercept= $C\text{-}1/g_m C + 1/g_m C - 1/g_m$

From the plot, the value of g_m can be obtained.

The constant C = (slope + 1)/Intercept is a measure of the difference in heats of adsorption of the 1st layer and the succeeding layers. The specific surface area is given by:

$$S, m^2/g = g_m .\ N \times B/m \times M$$

where

N = Avogadros No.;

B = molecular area of the adsorbate (benzene) = $41A^2 = 41 \times 10^{-20}$ m^2;

M = mass of the sample; and

M = molecular mass of benzene.

On substitution, we get, $S = g_m \times 3166/m$

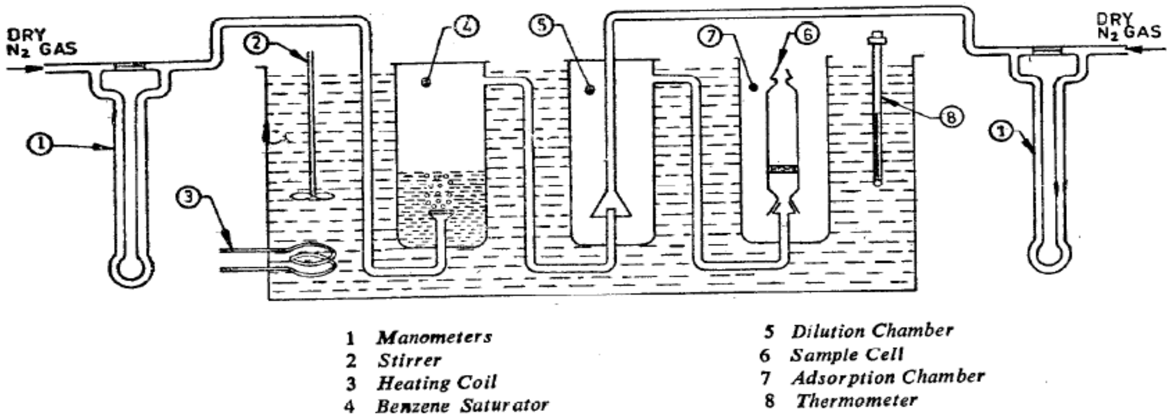

Fig. 1 Apparatus for Surface Area Measurement

ANNEX B

(*Foreword*)

COMMITTEE COMPOSITION

Inorganic Chemicals Sectional Committee, CHD 01

Organization	*Representative(s)*
Central Salt and Marine Chemicals Research Institute, Bhavnagar	Dr Kannan Srinivasan (***Chairman***)
Aditya Birla Chemical (I) Ltd, New Delhi	Shri Alok Singh
Alkali Mfrs Association of India, Delhi	Shri K. Srinivasan Shri Subhash Tandon (*Alternate*)
Bhabha Atomic Research Centre, Mumbai	Dr A. V. R. Reddy Dr S. N. Achary (*Alternate*)
Central Drugs Standard Control Organization	Dr Raman Mohan Singh
DGQA, New Delhi	Dr Gurbachan Singh Shri B. S. Tomar (*Alternate*)
Geological Survey of India, Kolkata	Dr D. K. Das Dr Subhas Chandra (*Alternate*)
Grasim Industries Ltd, Nagda	Shri R. S. Baghel Shri Pankaj Gupta (*Alternate*)
Gujarat Alkalies and Chemicals Ltd, Vadodara	Dr Sunil Sinha
Hindustan Lever Ltd, Mumbai	Vrindarajwade Shrimati Poornakala (*Alternate* I) Satyamoorthy (*Alternate* II)
In personal capacity	Dr A. N. Bhat
In personal capacity	Dr T. S. Kathpal
Industrial Carbon Pvt Ltd, Ankleshwar	Shri Rohit Kumar Madhavji Shri Satyan Rohit Kumar (*Alternate*)
Indian Institute of Chemical Technology, Hyderabad	Dr Praveen R. Likhar Dr Rajender Reddy (*Alternate*)
Ministry of Defence (DGQA), Kanpur	Shri R. N. Aparajit
Ministry of Chemicals & Fertilizers	Dr Rohit Misra
National Chemical Laboratory, Pune	Dr Darbha Srinivas Dr Paresh Dhepe (*Alternate*)
National Metallurgical Laboratory, Jamshedpur	Dr Trilochan Mishra Shri Devbrata Mishra (*Alternate*)
National Mineral Development Corporation Ltd, Hyderabad	Shri Rajan Kumar Dr Prashant Sharma (*Alternate*)
National Physical Laboratory, New Delhi	Dr Nahar Singh Dr S. P. Singh (*Alternate*)
National Test House (NR), -------	Dr Y. C. Nijhawan Dr (Ms) A. Biswas (*Alternate*)

Organization	*Representative(s)*
Nirma Chemicals, Ahmedabad	Shri R. A. Joshi Dr K. C. Pathak (*Alternate*)
Office of the Development Commissioner (MSME), New Delhi	Shrimati Shimla Meena Shri Santosh Kumar (*Alternate*)
Reliance Industries Ltd, Navi Mumbai	Shri Dhanavadan Modi
Shriram Institute for Industrial Research, Delhi	Dr (Ms) Laxmi Rawat Shri B. Govindan (*Alternate*)
VOICE, Delhi	Shri H. Wadhwa Shri K. C. Chaudhary (*Alternate*)
In Personal Capacity	Shri D. K. Jain
Vaibhav Analytical Services, Ahmedabad	Shri Gaurang Oza
BIS Directorate General	Shri A. K. Lal, Scientist 'E' and Head (CHD) [Representing Director General (*Ex-officio*)]

Member Secretary

Sagar Singh
Scientist 'C' (CHD), BIS

Bureau of Indian Standards

BIS is a statutory institution established under the *Bureau of Indian Standards Act*, 2016 to promote harmonious development of the activities of standardization, marking and quality certification of goods and attending to connected matters in the country.

Copyright

BIS has the copyright of all its publications. No part of these publications may be reproduced in any form without the prior permission in writing of BIS. This does not preclude the free use, in the course of implementing the standard, of necessary details, such as symbols and sizes, type or grade designations. Enquiries relating to copyright be addressed to the Director (Publications), BIS.

Review of Indian Standards

Amendments are issued to standards as the need arises on the basis of comments. Standards are also reviewed periodically; a standard along with amendments is reaffirmed when such review indicates that no changes are needed; if the review indicates that changes are needed, it is taken up for revision. Users of Indian Standards should ascertain that they are in possession of the latest amendments or edition by referring to the latest issue of 'BIS Catalogue' and 'Standards: Monthly Additions'.

This Indian Standard has been developed from Doc No.: CHD 01 (16255).

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

BUREAU OF INDIAN STANDARDS

Headquarters:

Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 110002
Telephones: 2323 0131, 2323 3375, 2323 9402 *Website*: www.bis.gov.in

Regional Offices: *Telephones*

Central : Manak Bhavan, 9 Bahadur Shah Zafar Marg
NEW DELHI 110002
2323 7617
2323 3841

Eastern : 1/14 C.I.T. Scheme VII M, V.I.P. Road, Kankurgachi
KOLKATA 700054
2337 8499, 2337 8561
2337 8626, 2337 9120

Northern : Plot No. 4-A, Sector 27-B, Madhya Marg
CHANDIGARH 160019
265 0206
265 0290

Southern : C.I.T. Campus, IV Cross Road, CHENNAI 600113
2254 1216, 2254 1442
2254 2519, 2254 2315

Western : Manakalaya, E9 MIDC, Marol, Andheri (East)
MUMBAI 400093
2832 9295, 2832 7858
2832 7891, 2832 7892

Branches : AHMEDABAD. BENGALURU. BHOPAL. BHUBANESHWAR. COIMBATORE. DEHRADUN. DURGAPUR. FARIDABAD. GHAZIABAD. GUWAHATI. HYDERABAD. JAIPUR. JAMMU. JAMSHEDPUR. KOCHI. LUCKNOW. NAGPUR. PARWANOO. PATNA. PUNE. RAIPUR. RAJKOT. VISAKHAPATNAM.

Published by BIS, New Delhi